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## XIII.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF  
THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XLVII. — CALORIMETRY: METHODS OF COOLING  
CORRECTION.

BY SILAS W. HOLMAN.

Presented November 13, 1895.

THE following general method of treating the cooling correction is applicable to nearly all non-continuous calorimetric processes, such as the measurement of specific heats by the "method of mixture," of heat of combustion by the Berthelot or Mahler bomb, etc. It is reliable in ordinary practice within the limits of error imposed by the thermometry and by irregularity of conditions as to surroundings.

Following the brief statement of the "General Method" is that of a "special case" of that method, and of a "Modified Method." These are supplemented by a demonstration of the "Theory of the Methods," and a "Critique."

The procedure in the modified method is supposed to be new. Beyond that fact this paper claims the attention merely of those who desire a concise working statement of a method of cooling correction which has stood the test of practice.

GENERAL METHOD.

*Procedure.* — Start with the water of the calorimeter at any convenient temperature, e. g. about that of the air. If there is a water jacket around the calorimeter, let that be stirred thoroughly once for all, or, better, continuously. Record its temperature at the beginning and end of the measurements as a possibly useful check.

Let the water of the calorimeter be stirred thoroughly, continuously, and at a uniform rate. Record times and temperatures of the

calorimeter each half-minute until the completion of the measurements (quarter-minute readings are sometimes preferable). After five or more minutes, at a noted time, drop in the hot substance, or start the calorimetric operation, whatever it may be, continuing the tempera-

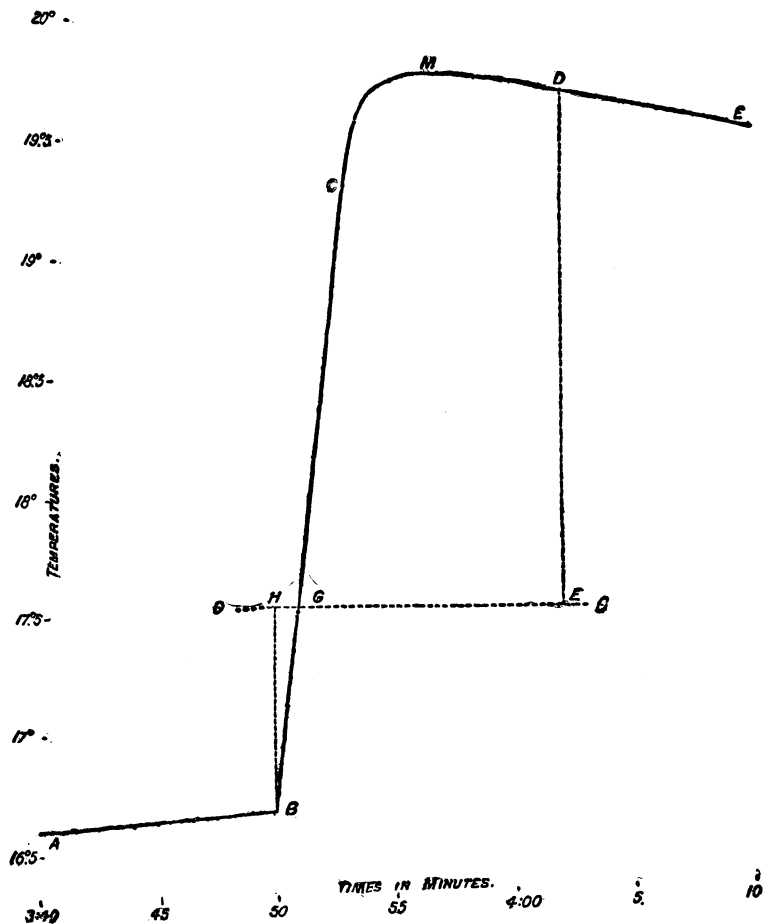


FIG. 1.

ture reading throughout the operation, and for at least five (better ten) minutes after its completion. The plot shows a typical set of observations.

A few readings may unavoidably be missed, where there is but one operator, viz. at the time *B* and in the steep part of *BC*; but

these are unimportant, since the former can be obtained by prolonging the line through the data preceding the omission, and the steep part of  $BC$  can be drawn in by judgment accurately enough because of the fact that it is of so short duration, and must be nearly straight.

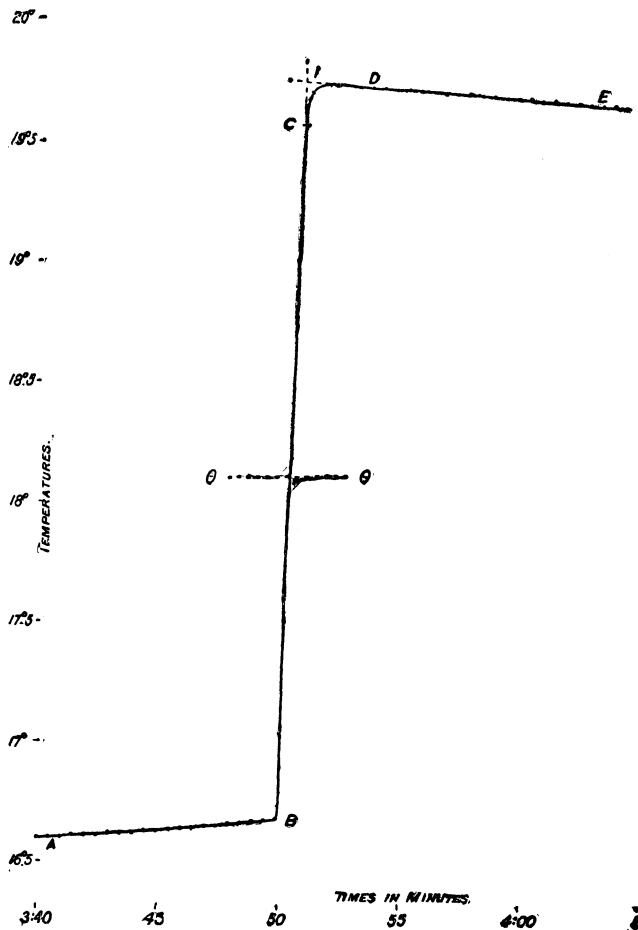


FIG. 2.

*The Correction.*— The significance of the terms given in this summary will appear on reading the “Theory of the Methods.” From a plot, or from the data direct, find the initial rate  $r_1$  and the temperature  $t_1$  at the time  $m_1$ ; also the final rate  $r_2$  and temperature  $t_2$  at  $m_2$ .

From the plot or data compute the mean calorimeter temperature for the time interval  $m_2 - m_1$  by the expression

$$T = \frac{1}{n-1} \left[ \frac{1}{2} t_1 + b + c + \dots + \frac{1}{2} t_2 \right],$$

where  $n$  is the number of half-minute temperature readings  $t_1, b, c, \dots, t_2$ . Compute also

$$a = \frac{r_1 - r_2}{t_2 - t_1}, \text{ and } \theta = \frac{r_2}{a} + t_2, \text{ or } = \frac{r_1}{a} + t_1.$$

Then the corrected rise of temperature in the calorimeter will be

$$t_2 - t_1 + a (T - \theta) (m_2 - m_1),$$

or if the area method is adopted,

$$t_2 - t_1 + a A.$$

*Special Case.* — Where  $BC$  is sensibly straight, and  $CM$  (Fig. 1) is of short duration relatively to  $BC$ , then  $t_2$  is to be found by prolonging  $ED$  (Fig. 2) to its intersection in  $I$  with the vertical through  $C$ , the point where the operation ceased, or where  $BC$  begins to deflect from a straight line. From  $C$  onward the exchange has been at the rate of  $DE$ ; hence the ordinate of  $I$  may be taken as the temperature which would have been indicated had all the remaining heat been distributed throughout the calorimeter instantly when the operation ceased. This may be called  $t_2$ . The gain by exchange during the passage from  $B$  to  $C$  is obviously about  $\frac{1}{2} (r_1 + r_2) (m_2 - m_1)$ , where  $m_2$  is the time corresponding to  $t_2$ . The corrected rise of temperature is then

$$t_2 - t_1 - \frac{1}{2} (r_1 + r_2) (m_2 - m_1).$$

Whether this special method is close enough can be determined for any series of measurements by solving a typical example both by it and by the general method.

#### MODIFIED METHOD.

*Procedure.* — By computation from approximate or estimated values of the quantities involved, or from a preliminary trial, determine nearly what the rise of temperature in the calorimeter is to be and call this  $\Delta t$ . Start with the water of the jacket at, or a degree or two above, the temperature of the air of the room. In the calorimeter, start with the water  $\Delta t^\circ$  below that of the jacket, or enough more than

$\Delta t$  to allow for unavoidable rise during preliminary manipulations, — in short, so that  $t_1^\circ$  shall be as nearly as may be  $\Delta t^\circ$  lower than  $\theta^\circ$ . The object of this is to have  $t_2$  so nearly  $\theta$  that  $r_2$  shall be nearly zero. On the plot of observations, Figure 1, this would cause  $AB$  to incline upwards and  $DE$  to become nearly horizontal.

Then proceed precisely as in the general method, both as to manipulation and computation.

#### THEORY OF THE METHODS.

A typical set of readings obtained under the general method, corrected for thermometric error, and plotted with times as abscissas and temperatures as ordinates, would lie along a line  $ABCDE$ , Figure 1. This curve should be convex upward all the way from  $C$  to  $D$ , there becoming straight. If any concavity shows itself between the maximum  $M$  and  $E$ , or if the straight line through the points between  $D$  and  $E$  cuts the curve anywhere between  $C$  and  $D$ , then the data should be rejected. For the inference, almost without exception, is that the stirring was insufficient to keep the thermometer down to the average calorimetric temperature. This may be due either to the bulb being badly located, so that it is unavoidably heated to excess, or merely to ineffective stirring. The difficulty should be removed, and the observation repeated.

The line consists of four portions, viz.: 1. The preliminary readings,  $A$  to  $B$ . 2. The readings during the operation,  $B$  to some indeterminate point  $C$ . 3. Readings  $C$  to  $D$  while the calorimeter and contents are becoming equalized in temperature. 4. Final readings after this equalization has become sensibly completed, and the calorimeter and contents are cooling, or heating, by exchange with their surroundings. In many cases, as in specific heat determinations, the second and third parts are one; that is, the operation is the equalization of temperature between the calorimeter and the substance introduced into it. In the case of a combustion and many other operations these two parts are to be distinguished.

The method is based upon Newton's law of cooling. Test observations have shown that this law holds with sufficient accuracy for both open and closed calorimeters, that is, within the uncertainty attributable to varying conditions of surroundings and to thermometric errors.

From the best representative straight line drawn through the observed points between  $A$  and  $B$  is deduced the initial rate of exchange,

$r_1$  (positive for a rising, negative for a falling temperature), expressed in degrees per minute.

For the data between  $D$  and  $E$ , i. e. through the observations for the final few minutes, which will lie sensibly along a straight line, is deduced similarly the final rate  $r_2$ .

Let  $t_1$  be the temperature at the point  $B$ , the beginning of the operation. Call this the initial temperature. Then  $r_1$  is the exchange rate at  $t_1$ . Let  $m_1$  be the corresponding time. Let  $t_2$  be the temperature at the earliest minute or half-minute at which the line has become straight, that is, at which the fourth stage has been sensibly attained, e. g. the point  $D$ . Call this the final temperature of the calorimeter, and  $m_2$  the corresponding time in minutes. Then  $r_2$  will be the rate at  $t_2$ .

The average temperature of the calorimeter between  $m_1$  and  $m_2$  is next found as follows. Drawing through the points the best representative line  $B C M D$ , read off its ordinates at each half-minute (better each quarter-minute) from  $m_1$  to  $m_2$ . Instead of a plot the corrected data may be used directly. Call these temperatures  $a (=t_1)$ ,  $b$ ,  $c$ ,  $d$ , . . . ,  $n (=t_2)$ , then the average temperature will be

$$T = \frac{1}{n-1} \left[ \frac{a}{2} + b + c + \dots + \frac{n}{2} \right] = \frac{1}{n-1} \left[ \frac{1}{2} t_1 + b + c + \dots + \frac{1}{2} t_2 \right].$$

This is, of course, the well known process. A slightly better one is to read off the temperature at the end of the first *quarter*-minute after  $m_1$ , then at intervals of a *half*-minute (viz. at  $\frac{3}{4}$ ,  $\frac{5}{4}$ , etc.) up to  $m_2$ , which must therefore be selected at a point an even number of quarter-minutes from  $m_1$ , as there must be a quarter-minute interval at each end. The average of these also gives  $T$ .

By Newton's law of cooling, the rate of gain or loss of heat by a body through exchange with surroundings is directly proportional to the difference of temperature between the body and the surroundings. In calorimetry, provided that the heat capacity of the calorimeter and contents is not changed materially during the process (by the insertion or removal of substances), the rate of gain of temperature through exchange is proportional to the rate of gain of heat, so that the cooling correction may be applied directly to the temperature, instead of to the heat.

Under this condition, the rate of exchange of temperature when the calorimeter is at any temperature  $t$  will be

$$r = a (t - \theta),$$

where  $\theta$  = some constant temperature (representing that of the surroundings, which may not be uniform or known) and  $a$  = the rate per degree difference between  $\theta$  and  $t$ .

The two quantities  $a$  and  $\theta$  are unknown, but obviously can be computed from the two pairs of observed values,  $r_1, t_1$ , and  $r_2, t_2$ . For

$$r_1 = a (\theta - t_1); \quad r_2 = a (\theta - t_2);$$

$$a = \frac{r_1 - r_2}{t_2 - t_1};$$

$$\theta = \frac{r_2}{a} + t_2, \quad \text{or} \quad \frac{r_1}{a} + t_1.$$

Both  $a$  and  $\theta$  are next computed numerically from the data.  $\theta$  is best found from the smaller value of  $r$ , for the reason that it influences the result most largely through its subsequent combination with values near that one.

The gain of temperature by exchange, then, in any short interval of time,  $\Delta$ , during which the temperature is  $t$ , will be  $a (\theta - t) \Delta$ .

The rate of gain of temperature is  $a (\theta - t)$ , or  $a \theta - a t$ , so that, as  $\theta$  is constant,  $r$  varies directly as  $t$ . Hence the average rate will be proportional to the average value of  $t$ , that is, to  $T$ , and will be  $a \theta - a T$ , or  $a (\theta - T)$ . The total gain will therefore be this quantity multiplied by the duration ( $m_2 - m_1$ ) of this average rate, or  $a (\theta - T) (m_2 - m_1)$ , and the exchange (or "cooling") correction will be this with reversed sign, viz. :

$$-a (\theta - T) (m_2 - m_1), \quad \text{or} \quad a (T - \theta) (m_2 - m_1).$$

The corrected rise of temperature of the calorimeter will then be

$$t_2 - t_1 + a (T - \theta) (m_2 - m_1).$$

Obviously  $(T - \theta) (m_2 - m_1)$  is the area  $HCOFH$  minus the area  $BGH B$ . This difference,  $A$ , in proper units, may therefore be measured on a plot by the planimeter or otherwise, and the corrected temperature rise will then be

$$t_2 - t_1 + a A.$$

#### CRITIQUE OF THE METHODS.

Three assumptions, beyond that of Newton's law of cooling, are involved in the employment of this method, unless otherwise provided for in the computations into which the corrected rise of temperature is introduced. First, that the thermometer indicates the



surface temperature of the calorimeter. Secondly, that the temperature distribution throughout the entire contents of the calorimeter is uniform both when  $r_2$  and  $r_1$  are taken, so that these are really rates of exchange with surroundings, and not resultants in which the desired rate is more or less modified by redistribution within the calorimeter. Thirdly, that the heat capacity of calorimeter and contents is the same both when  $r_1$  and  $r_2$  are taken.

Proper location of thermometer, efficient stirring, and the prevention of direct contact with the calorimeter of any hot or cold object within it, readily insure the fulfilment of the first with sufficient closeness.

Wherever the temperature of the calorimeter is varying, uniform distribution of temperature throughout its contents is obviously impossible if these are heterogeneous, especially where there is a large metallic mass surrounded by the water, as the bomb in the Berthelot or Mahler combustion apparatus. Such objects will necessarily lag more or less behind the water as the temperature of the latter falls or rises by external exchange. The effect of this is to falsify the apparent rate  $r_1$  or  $r_2$ , and still further to vitiate the results through the usual assumption that all parts are at the same temperature. A form of cooling correction, taking this into account and applying to a certain class of cases, has been described by Professor Rowland, but the only method which could entirely eliminate the error would be to arrange the calorimetric process so that the rate of exchange should be sensibly zero or constant during the entire measurement. This means that the jacket temperature must be so controlled as to be always at the temperature of the calorimeter, or at a constant difference from it. While this at first sight appears wholly impracticable, and is so for most cases, I am disposed to think that it might be feasible and helpful in certain investigations, such as the study of the specific heat of water, and the mechanical equivalent of heat, using electrical methods of heating, combined with thermoelectric means of detecting and controlling the temperature difference between the calorimeter and jacket.

The "Modified Method" described above deals with this error in another way. It makes the final rate  $r_2$  as nearly as possible zero, and hence secures the greatest possible constancy of temperature during the portion  $CDE$  of the curve when the rate is about  $r_2$ . The advantages gained are as follows. The apparent rate  $r_2$  is sensibly the true rate, since it will in general be much less than the rate of redistribution of heat amongst the contents of the calorimeter. This

is of vital importance to freedom from constant or systematic error, because the duration of the rate  $r_2$  is inevitably greater, often much greater, than of any other rate. If, as in the usual process, therefore, it is a large (often the largest) and the least accurately known rate, it is obviously productive of the most serious part of the error of the cooling correction. The modified method does not increase the lapse of time preceding the arrival of the final steady condition,  $D$ , which must in all methods, directly or indirectly, be the basis from which to deduce  $t_2$ . And as it does increase the percentage reliability of  $r_2$ , and reduces its amount, it diminishes the total amount of the correction, thus in a twofold way improving the result. The gain for operations of such a nature that the duration of  $C D$  is several or many times that of  $B C$  is large, being approximately in proportion to those durations. Into that category would fall many of the ordinary calorimetric processes, all those resembling the measurement of specific heats of liquids which cannot be mixed with that of the calorimeter, the use of the bomb for heats of combustion, and almost all processes involving the presence of considerable metallic or glass apparatus within the calorimeter. The method is of much less advantage where the duration of  $C D$  is brief.

In certain cases there is a slight offsetting increase of error in  $r_1$ , namely, when the contents are heterogeneous when both  $r_1$  and  $r_2$  are taken. This occurs in the case of the bomb, but not that of the specific heats of liquids or solids. For then  $r_1$  is a larger rate, and is inaccurate from the cause under consideration. Inasmuch, however, as this rate has during the operation  $B C$  only a relatively short existence, and its error as affecting the value of  $a$  is divided by  $(t_2 - t_1)$ , the error introduced by it is small. It should be noted that if the calorimeter is used as a secondary apparatus, not as a primary or absolute one, the systematic parts of the above errors are further reduced. Thus, for instance, in using the bomb, the heat capacity of bomb, calorimeter, and entire contents may best be ascertained by burning in it a known mass of some pure substance of well determined heat of combustion (e. g. naphthalin), and computing backward from that heat to find the total capacity. This makes the apparatus a secondary one, dependent upon the assumed heat of combustion, but it is much safer than computing the capacity from the assumed specific heats and the masses of the component parts, or than measuring it by the addition of warm water in the well known manner.

Departure from the third assumption above named cannot be discussed in detail, since the effect varies widely with the change of vol-

ume and exposed surface, as well as of heat capacity of the contents of the calorimeter in each case. Whether the change of capacity is sufficient to demand allowance can be usually determined by inspection of the case, and a special method of treatment provided. The usual effect is to make the apparent value of  $r_2$  smaller relatively to  $r_1$  than would correspond to Newton's law.

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